Dynamics of Volatile Sulfur Compounds and Volatile Organic Compounds in Sewer Headspace Air

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Abstract

A two year monitoring study was conducted at a sewer pumping station to investigate volatile sulfur compound (VSC) and volatile organic compound (VOC) emission dynamics over a range of timescales to gain an understanding of how they impact the design and execution of sewer odorant monitoring. It was demonstrated that the sewer system was highly dynamic and influenced by a range of processes at different time scales. Based upon odour activity values, hydrogen sulfide and methyl mercaptan had strong potential to be odorous, while dimethyl sulfide and dimethyl disulfide were potentially odorous at source concentrations. In general VOCs were not likely to be odorous at source concentrations, although some episodic elevations in aromatic hydrocarbon and terpene concentrations to potentially odorous levels were observed and as a result VSCs are the primary targets for sewer odour abatement. A strong diurnal emission cycle was observed, with dynamic ranges (ratio of peak to average concentration) between 2.34 and 4.55 for specific VSCs and 1.82 to 10.6 for specific VOCs. Interday variability over a one week period was relatively low for many VSCs, with coefficients of variance generally ranging from 11% to 30%, while VOC emissions had greater variability, with coefficients of variance ranging from 29% to 220%.

Introduction

The installation and operation of gas phase odour abatement technology on sewer networks represents a significant investment by utility operators (Estrada et al. 2012; Estrada et al. 2011; Smet et al. 1998) to minimise odour emissions while providing an essential waste management service. Two risks in selecting and installing these technologies are their suitability to abate the specific odorants being emitted, and the level of abatement performance. Obtaining information with regards to the types and concentrations of odorous compounds being emitted is a key step to manage these risks. With a wide range of potential odorants and associated analytical/sampling methodologies, the cost of obtaining a full characterisation of odorant emissions from sewers can be cost prohibitive and in most cases a small number of grab samples are collected to describe odour and odorant emissions (Sivret and Stuetz 2010).

Existing studies have explored the range of volatile sulfur compounds (VSCs) and volatile organic compounds (VOCs), with most studies focusing on the type and concentrations (Chan and Hanaeus 2006; Corsi et al. 1995; Haas and Herrmann 1996; Huang et al. 2012; Kangas et al. 1986; Thistlethwayte and Goleb 1973; Wang et al. 2014) present in sewer networks. Other work (Burlingame et al. 2004; Decottignies et al. 2013) has focused on describing the characteristics of the odours of the VOCs/VSCs present, but there is minimal published literature exploring the dynamics of odorants in sewer headspaces.

A two year monitoring study was conducted at a sewer pumping station located in Sydney, Australia to address this knowledge gap and provide information to support efficient and cost effective sewer odorant monitoring practices leading to enhanced

70 odour abatement process design and performance. The goals of this study were to
71 investigate the emission dynamics of VSCs and VOCs over a range of timescales to
72 understand how they impact the design and execution of sewer odorant monitoring.

Monitoring Program - Materials and Methods

The monitoring program used to generate the data necessary for this study was conducted at a pumping station wet well in Sydney, Australia. The sewer line to the pumping station is a 1200 mm reinforced concrete pipe with an average dry weather flow of 0.13 ML/day. The sewage in the sewer has been collected from an urban catchment (mixed sewage consisting of both domestic and trade waste), and there is no liquid phase chemical dosing in the portion of the sewer network studied. Stormwater is collected and managed via a separate stormwater system, although infiltration does occur during rain events.

The monitoring program was split into two components; a lower intensity long term monitoring program to capture the long timescale dynamics and a more intensive short term monitoring program to capture short timescale dynamics. Both monitoring programs focused on identifying and quantifying the range of VOCs and VSCs present in the air being extracted from a pumping station. As the entire pumping station was enclosed, a single sample point on the exhaust leading to the odour abatement process provided a sample of the VOCs and VSCs from the air inside the wet well and the sewer headspace air entering the pumping station. Due to the enclosure, the emissions from the pumping station were not influenced by wind speed.

The long term monitoring program was conducted over a two year window between January 2011 and June 2013. Duplicate VOC and VSC samples were collected during each sampling event on a weekly basis during between January and March, which is the summer period during which peak odour emissions are commonly

reported by utility operators. Samples were collected at a reduced frequency (biweekly to monthly) during the rest of the study period. To reduce the potential impact of shorter term dynamic patters, to the maximum extent practical, samples were collected on the same day of the week (Wednesdays) and around a similar time window (10 am to 2 pm) throughout the monitoring program. A total of 29 and 23 sample events occurred for VOCs and VSCs, respectively, for a total of 58 VOC and 46 VSC samples being collected and analysed.

An intensive short term monitoring program was conducted over an 8 day period to assess emission dynamics on a day to day timescale and an hourly timescale. The monitoring program consisted of an initial 24 hour period of intensive sampling during which integrated air samples were collected over each 2 hour period in duplicate (a total of 24 VOC and 24 VSC samples were collected). Sampling was then conducted on a daily basis, with the each day of sampling consisting of 3 sampling events where integrated air samples were collected over each 2 hour period from 10 am to 4 pm to capture the expected peak concentration period. Samples were collected day 1 (corresponding with the diurnal study) and again on days 2, 3, 6, 7, and 8. Samples were not collected on days 4 and 5 due to the site not being accessible on Saturdays and Sundays. A total of 36 VOC and 36 VSC samples were collected and analysed for this part of the study.

Volatile Organic Compounds (VOCs) Sample Collection and Analysis

VOC samples were collected via absorption of the air into Tenax TA sorbent tubes (Markes International, UK). Samples were collected at a constant flow rate of 100 ml/min for 10 mins (1L sample volume) using a calibrated air sampling pump (SKC

Inc., USA). All of the sorbent tubes were conditioned (TC-20, Markes International, UK) and verified contaminant free prior to being used in the study.

Following transport to the laboratory, the sorbent tubes containing the VOC samples were thermally desorbed using a Unity thermal desorber (Markes International, UK) coupled with an Ultra automatic sampler (Markes International, UK). A general purpose cold trap (U-T11PGC, Markes International, UK) was used to collect the sample prior to injection into a gas chromatograph equipped with a mass spectrometer detector (7890N GC and 5975MSD, Agilent Technologies, USA). A DB-VRX column (Agilent Technologies, USA) was used for compound separation in the gas chromatograph. A helium carrier gas was used (1.8 ml/min flow) and the gas chromatograph column temperature was initially held at 50°C for 2 mins, raised at 15°C/min to 220°C, and then held for 3 minutes. The mass spectrometer was operated in continuous scan mode to maximise the range of VOCs identified. Standards of specific VOCs were used to develop the calibration curves necessary to quantify the VOC concentrations in the air samples (Wang et al. 2012).

Volatile Sulfur Compounds (VSCs) Sample Collection and Analysis

Whole air samples (5 L) were collected into Nalophan sample bags using a lung sampler. Nalophan bags were used due to their availability and low cost, and have been previously demonstrated to provide an acceptable level of performance when compared to other bag materials (Le et al. 2013; Le et al. 2015). The samples were then transported to the laboratory and analysed within 24 hours of collection to reduce VSC loss due via transformation, permeation through the bag, or adsorption onto the bag surface (Le et al. 2013; Le et al. 2015).

The VSC samples were connected to an Air Server (CIA 8, Markes International, UK) and the VSCs were adsorbed onto a specialised sulfur cold trap (U-T6SUL, Markes International, UK) prior to injection into a gas chromatograph equipped with a sulfur chemiluminescence detector (7890N GC and 355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA). A DB-VRX column (Agilent Technologies, USA) was used for compound separation. A helium carrier gas (1 ml/min flow) was used in the gas chromatograph and the column temperature was initially held at 37°C for 3 mins, raised at 15°C/min to 225°C, and held for 2 minutes. VSC standards were used to identity the sulfur peaks via retention time matching and to prepare the calibration curves required to provide quantitative data (Wang et al. 2015).

H_2S concentrations could not be quantified using the sulfur chemiluminescence detector due to the type of cold trap utilised in the methodology. H_2S concentrations were instead measured using a calibrated Jerome 631-X Hydrogen Sulfide Analyzer (Arizona Instrument, USA).

Results

Long Term Monitoring

The results of the monitoring were compiled for a suite of VOCs and VSCs identified in the collected samples. Odour activity values (OAV), the ratio of the compound concentration to the corresponding odour threshold value, were determined using a single set of odour threshold values (OTVs) (Nagata 2003). The single set of values was applied to provide a consistent benchmark as a wide range of OTVs exist (van Gemert 2003) with significant variation in values. The Nagata (2003) results represent modern olfactory analysis techniques and provide a reasonably comprehensive set of OTVs for compounds of interest. One notable gap is the lack of an OTV for dimethyl trisulfide.

Concentration and OAV data for VSCs over the study period are presented in Fig. 1. A tabulated dataset with specific VSC concentrations, OAVs and meteorological data have been provided as supplementary material (Table S1). Significant variability in VSC concentration is observable between sampling events. Considering the OAVs provides a more consistent picture, with hydrogen sulfide and methyl mercaptan having high OAVs (100 to 10000, strong potential to be odorous). Dimethyl sulfide and dimethyl disulfide OAVs were around or greater than 1 and are potentially odorous at source strength. The carbon disulfide OAV was less than 0.1 and is not likely to be odorous. Ethyl mercaptan, diethyl sulfide, diethyl disulfide, diethyl trisulfide, and carbonyl sulfide were only detected in a very small number of sampling events.

The seasonal fluctuation in average daily maximum temperatures (Fig. 2) appear to be represented to some extent in the VSC concentrations (although more visible in the OAV values) presented in Fig. 1. There were much higher rainfalls in 2011 than 2012 (Fig. 2), but the expected suppressive effect was not strongly visible in the data.

The measured VOC concentrations along with the OAVs (provided in Tables S2 and S3 and illustrated in Fig. S1 and S2 in the supplementary material) had strong variability in some cases. The seasonality/ meteorological influence on VOCs was not consistent. Increased concentrations were observed during the first summer (end of 2011 and early 2012), but a very flat concentrations profile was observed during the remainder of 2012 and the following summer.

VOC OAVs were generally less than 1. As a result, most VOCs are not likely to be odorous at source concentrations and they are not primary odorants.

Short Term Monitoring

The short term monitoring program was conducted during October 2013. This was a relatively dry month, with a total of 16.5 mm of rain falling and no rainfall for the 8 days prior to the monitoring program. Four small precipitation events occurred during the monitoring period, 3.8 mm on Day 1 (which corresponds to the second half of the diurnal study), 1.2 mm on day 6, 5.2 mm on Day 7, and 0.6 mm on Day 8. The day to day variability of VSC and a representative set of VOC OAVs are provided in Fig. 3 and Fig. 4, respectively. Concentration and OAV data for the full range of compounds studied are provided in the supplementary material as Table S4 for

VSCs and Tables S5 and S6 for VOCs. The daily variability for other VOCs are illustrated in Fig. S3 as there was a relatively similar ordering of the compounds in terms of OAV for similar times over the 6 sampling days.

A diurnal VSC cycle was observed (Fig. 5), with the lowest VSC concentrations and OAVs occurring around 4 am and concentrations increasing during the daytime to a peak in the early/late evening and then dropping overnight. A similar pattern was observed for VOC concentrations in Fig. S4 and S5.

Specific VSC and VOC concentration data were analysed to explore the shorter term dynamics present at the site being studied (Table 1). This analysis focused on potential variability during a diurnal cycle and daily variability, both useful information for determining the capacity required for odorant abatement and for monitoring campaign design.

The dynamic range (ratio of peak to average concentration) for VSCs on a diurnal basis was between 2.34 and 4.55. The dynamic range for VOCs was wider (ranging from 1.82 to 10.6), with alkanes having the greatest dynamic range. No correlation was observed between the dynamic range and specific compound molecular weight or boiling point.

The interday variability over the 8 day period studied (6 sampling events) was relatively low for VSC emissions, with coefficients of variance ranging from 11% to 30%. VOCs had higher interday variability, generally ranging from 29% to 220%. No

239 correlations were observed between interday variability and VOC family, molecular
240 weight, or boiling point.
241

Discussion

The goals of this study were to investigate the emission dynamics of volatile sulfur compounds (VSCs) and volatile organic compounds (VOCs) over a range of timescales to understand how they impact the design and execution of sewer odorant monitoring. The study was successful in capturing some of the long term VSC variability/dynamics associated with climate. The higher odorant concentrations were associated with warmer and/or dryer periods. VOC emissions did not appear to have the same level of association. This is likely due to differences in the origins of the two compound groups. While both VOCs and VSCs originate from biological processes within the sewers (Hvitved-Jacobsen et al. 2002; Rudelle et al. 2011), many VOCs are also associated with domestic and/or trade waste discharges (Haas and Herrmann 1996; Haas and Herrmann 1998; Nikolaou et al. 2002).

The scatter in much of the long term data is likely the result of strong short term dynamic events such as weather events, diurnal human activity patterns, and periodic discharge events that overlap the long timescale dynamics. An example of the suppressive effect of a rainfall event on sewer emissions showed nearly a 50% drop in odour concentration within 6 hours (Sivret et al. 2014). A higher sampling frequency and further understanding of the types and forms of short term dynamics is required to screen out their influence and further define the long term odorant concentration variability.

This study has a number of implications with regards to the design of monitoring programs to characterise sewer odorants to support the selection and design of odour abatement processes. First, it has been shown that sewers are a highly

dynamic system in terms of odorant generation and are influenced by a range of processes occurring in many different time scales. Second, to completely characterise the impact of each process is not a practical goal since it would require a high monitoring intensity and the cost/effort involved could dwarf that of the small odour abatement systems commonly applied on sewer networks. Third, the results are expected to be site specific since. Many of the parameters of influence are catchment and system specific parameters. These include land use, industrial/commercial activity, and physical sewer geometry in the form of structures and the ability to buffer rainfall/infiltration (Wang et al. 2014). While the results of a single study may provide some insight of what might be expected at similar sites, they cannot be reliably extended to these sites for design purposes. Finally, as VOCs were not likely to be odorous at source concentrations, VSCs were the primary targets for sewer odour abatement. The fate and impact of VOCs in odour abatement technologies has not yet been fully explored and further work is needed to determine their importance from that perspective before they are omitted form monitoring programs.

Existing studies have demonstrated the range of VSCs (Chan and Hanaeus 2006; Kangas et al. 1986; Thistlethwayte and Goleb 1973; Wang et al. 2014) and VOCs (Corsi et al. 1995; Haas and Herrmann 1996; Haas and Herrmann 1998; Huang et al. 2012) present in sewer networks. While there is variability from site to site with regards to specific concentrations and dominance of some of the compounds, there is consensus (Sivret et al. 2016) on the range of compounds that may be of interest . Tools also exist to explore previously acquired data to identify priority odorants; as seen in Fig. 1, odour activity values are a useful tool to extract coherent messages

292 from what can be a highly variable dataset from a concentration perspective. Despite
293 the significant variability in concentrations over the study period there is consistency
294 in which compounds are dominant odorants.
295
296 A probabilistic approach to monitoring campaign design focusing on clear monitoring
297 objectives is recommended to efficiently and cost effectively produce data to support
298 odour abatement process design. To minimise analytical cost the monitoring
299 objectives should clearly define what compounds are of importance and the specific
300 result required to support the odour abatement selection/design process. As the
301 processes/phenomena responsible for the emissions dynamics are for the most part
302 beyond direct control, this approach allows a balance to be chosen between the risk
303 of not achieving monitoring objectives and the scale (cost) of monitoring.
304
305 The monitoring program should then be structured to consider the typical dynamic
306 conditions to target the time periods with the highest probability of providing the
307 emission scenario desired. For example, if maximum emissions are the desired
308 design factor it would be recommended that the monitoring be conducted during the
309 late afternoon/early evening of a weekday during the summer with temperatures
310 near maximums preceding and during the monitoring period, without any significant
311 rainfall for several weeks prior to and during the monitoring.
312
313 While the long term dynamics are likely to be relatively easy to predict, the stronger
314 short term dynamics are likely to have a stronger influence on emissions (Fig. 5,
315 Table 1, and Sivret et al. 2014) and present a corresponding level of risk if not
316 accommodated in monitoring campaign design. It is recommended that the site be

317 screened for these dynamics to identify the optimal monitoring times for more
318 inventive investigation.
319
320 The final implication of this study is that context is particularly important when
321 comparing and interpreting sewer emission data presented in the literature. There is
322 a need to include the nature and operating conditions of the sewer networks,
323 weather, and climate as part of best practices by researchers and practitioners in the
324 future. This is of particular importance as the pool of available data will eventually
325 reach a size appropriate for consolidation and the application of meta-analysis tools.
326
327 A much longer (and likely more intensive) dataset would be required to capture even
328 longer timescale of dynamics such as population change or changes in land use
329 patterns. These dynamics were outside of the scope of the study and data was not
330 readily available from industry partners, however it would be useful information to
331 provide further context to the data.
332

Conclusion

VSC and VOC data collected over two year period from a sewer pumping station were analysed to explore long and short term concentration dynamics and provide better focus for monitoring campaign design. The higher odorant concentrations were associated with warmer and/or dryer periods. VOC emissions did not appear to have the same level of association. Longer timescale influences (population change and changes in land use patterns) were outside of the scope of the study.

Sewers were demonstrated to be highly dynamic system in terms of odorant generation and are influenced by a range of processes at different time scales. As many of the influencing processes are catchment and system specific parameters, results from a site cannot be reliably extended to other sites for design purposes. With these limitations, a monitoring program should be structured to consider typical dynamic conditions to target time periods with the highest probability of providing the emission scenario desired. Monitoring should also be based on an understanding of priority odorants and volatile compounds of interest

Context in terms of the nature and operating conditions of the sewer networks, weather, and climate were identified as being of particular importance to comparing and interpreting sewer emission data presented in literature. There is a need to include this information as part of best practices to enhance the value of the data and support meta style analysis in the future.

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Supplemental Data

Figs. S1 – S5 and Tables S1 – S6 are available online in the ASCE Library (ascelibrary.org).

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Figure Captions

Fig. 1. VSC concentrations (top) and OAVs (bottom) over study period

Fig. 2. Rainfall and temperature during study period

Fig. 3. Daily VSC OAVs

Fig. 4. Daily VOC OAVs – alkanes and halogenated hydrocarbons

Fig 5. Diurnal variability of VSC OAVs

Tables

Table 1. VSC and VOC diurnal and interday variability

Compound	Diurnal Variability				Interday Variability	
	Average Concentration (ug/m^3)	Peak Concentration (ug/m^3)	Minimum Concentration (ug/m^3)	Peak to Average Concentration Ratio	Mean Concentration ± Standard Deviation (ug/m^3)	Coefficient of Variance (%)
VOCs						
m,p-Xylene	7.85	15.1	0.30	1.93	35.0 ± 27.7	79.4
2-methylpentane	24.9	71.4	0.52	2.87	12.6 ± 21.4	170
α-Pinene	20.6	68.6	0.30	3.33	16.4 ± 15.0	91.4
Benzene, 1,4-dichloro-	154	288	71.7	1.87	393 ± 114	29.1
Cymene	59.2	290	0.31	4.91	5930 ± 6350	107
Decane	50.4	533	0.52	10.6	29.2 ± 64.1	220
Dodecane	21.5	101	0.52	4.70	57.6 ± 54.2	94.0
Ethylbenzene	2.30	8.96	0.30	3.90	20.0 ± 18.2	90.9
Ethylmethylbenzene	35.3	128	0.62	3.63	148 ± 146	98.4
Hexane	16.8	67.2	0.52	4.01	20.2 ± 36.3	179
Limonene	257	810	29.4	3.15	83.7 ± 134	160
Nonane	26.5	238	0.52	9.00	73.4 ± 70.3	95.8
o-Xylene	23.0	45.9	3.82	2.00	104 ± 87.4	84.0
Tetrachloroethylene	55.9	247	8.44	4.42	72.6 ± 38.6	53.1
Toluene	89.6	239	31.5	2.67	580 ± 828	143
Trichloromethane	925	1690	325	1.82	1720 ± 629	36.5
Trimethylbenzene	211	1020	0.31	4.81	1070 ± 793	74.1
TVOC	4850	9320	1730	1.92	19900 ± 10400	52.4
Undecane	54.5	345	0.52	6.32	139 ± 84.5	60.8
VSCS						
Carbon disulfide	6.67	18.9	2.04	2.83	6.85 ± 0.97	14.1
Dimethyl disulfide	42.0	132	7.89	3.15	29.5 ± 7.87	26.7
Dimethyl sulfide	57.7	147	19.8	2.55	45.8 ± 5.04	11.0
Dimethyl trisulfide	93.5	333	7.65	3.56	81.2 ± 24.1	29.6
Hydrogen sulfide	2140	5160	72.5	2.41	5360 ± 1220	22.8
Methyl mercaptan	178	808	1.15	4.55	255 ± 61.5	24.1
TVSC	4220	9900	630	2.34	6940 ± 1120	16.2

Fig. 1. VSC concentrations (top) and OAVs (bottom) over study period

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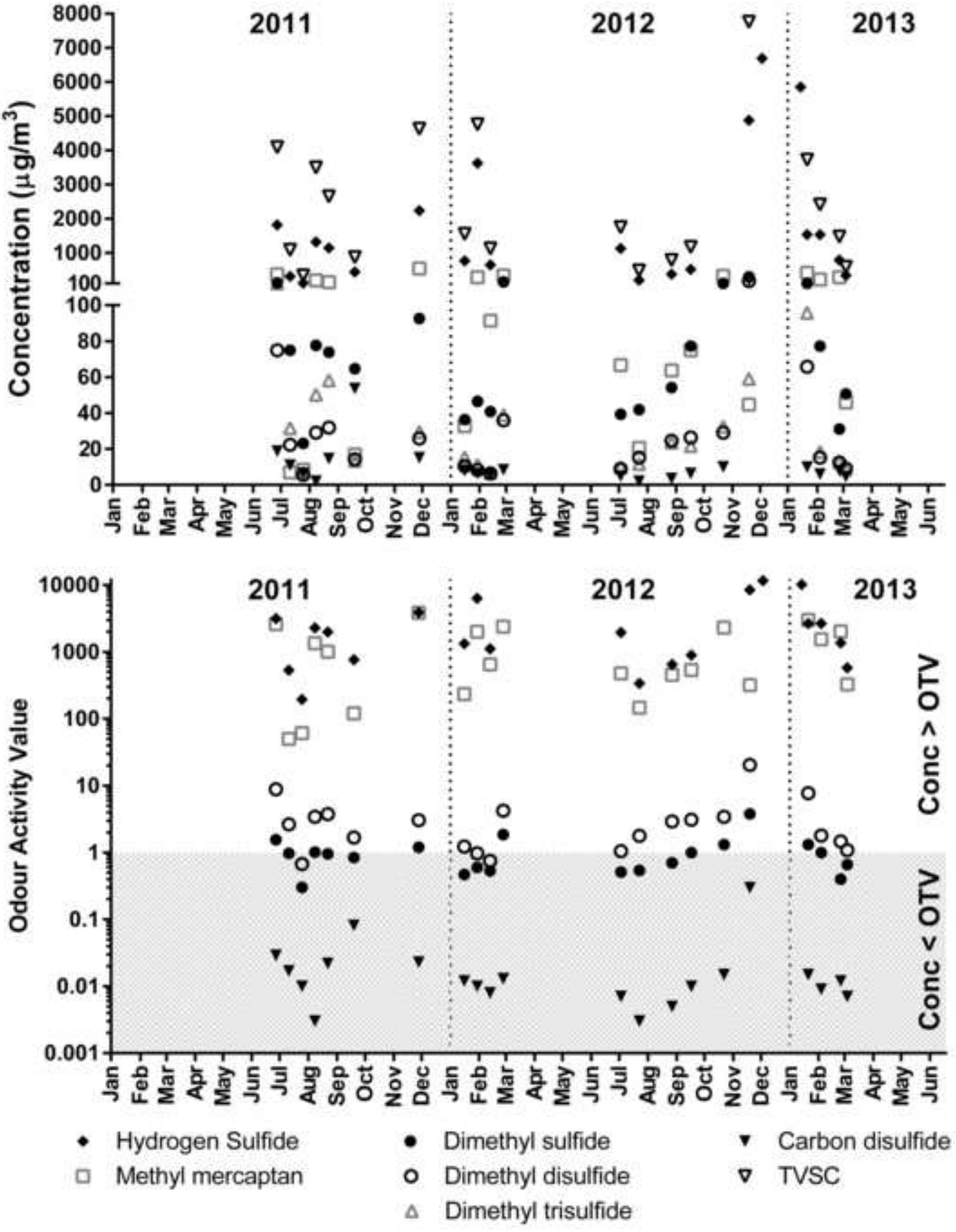

Fig. 2. Rainfall and temperature during study period

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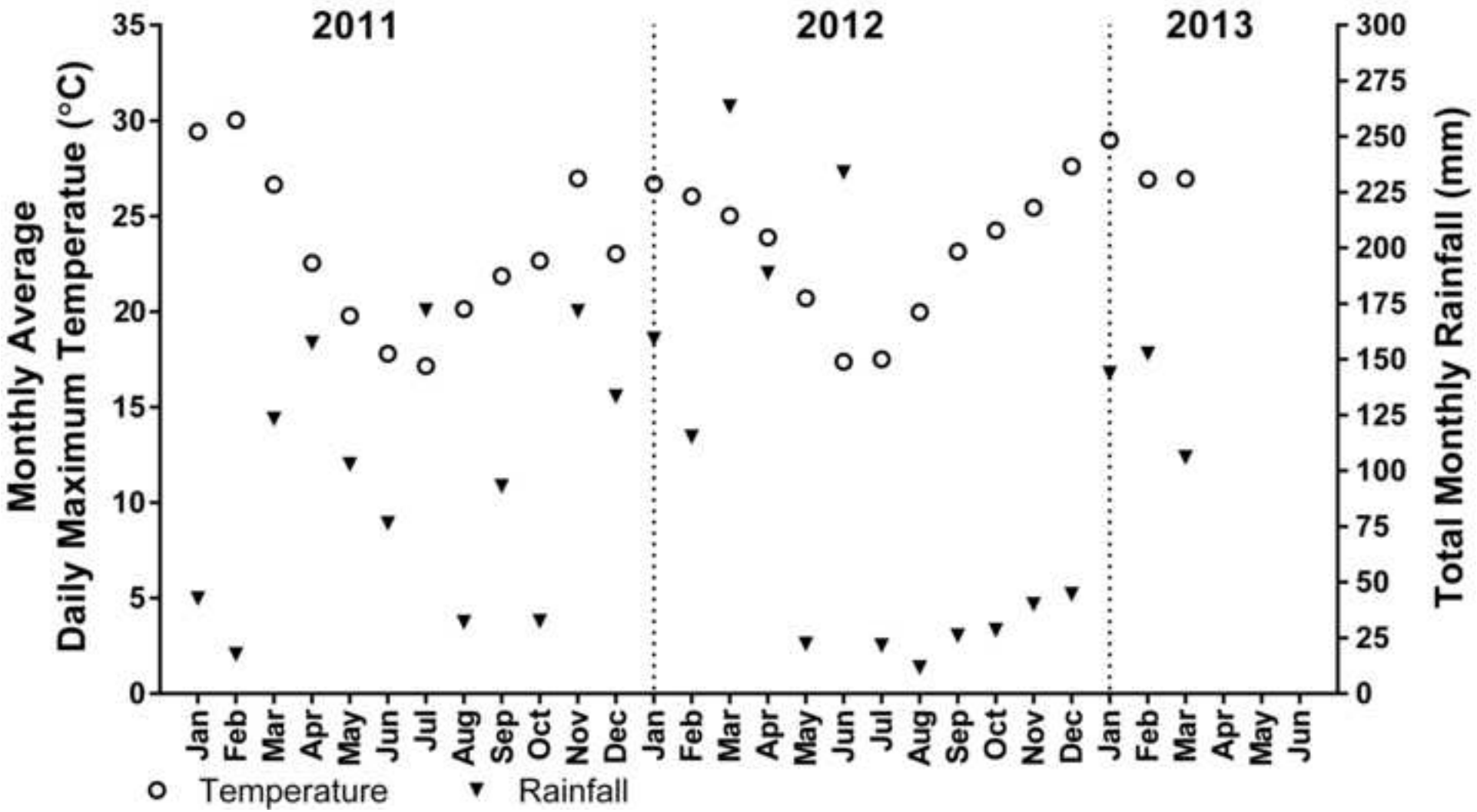

Fig. 3. Daily VSC OAVs

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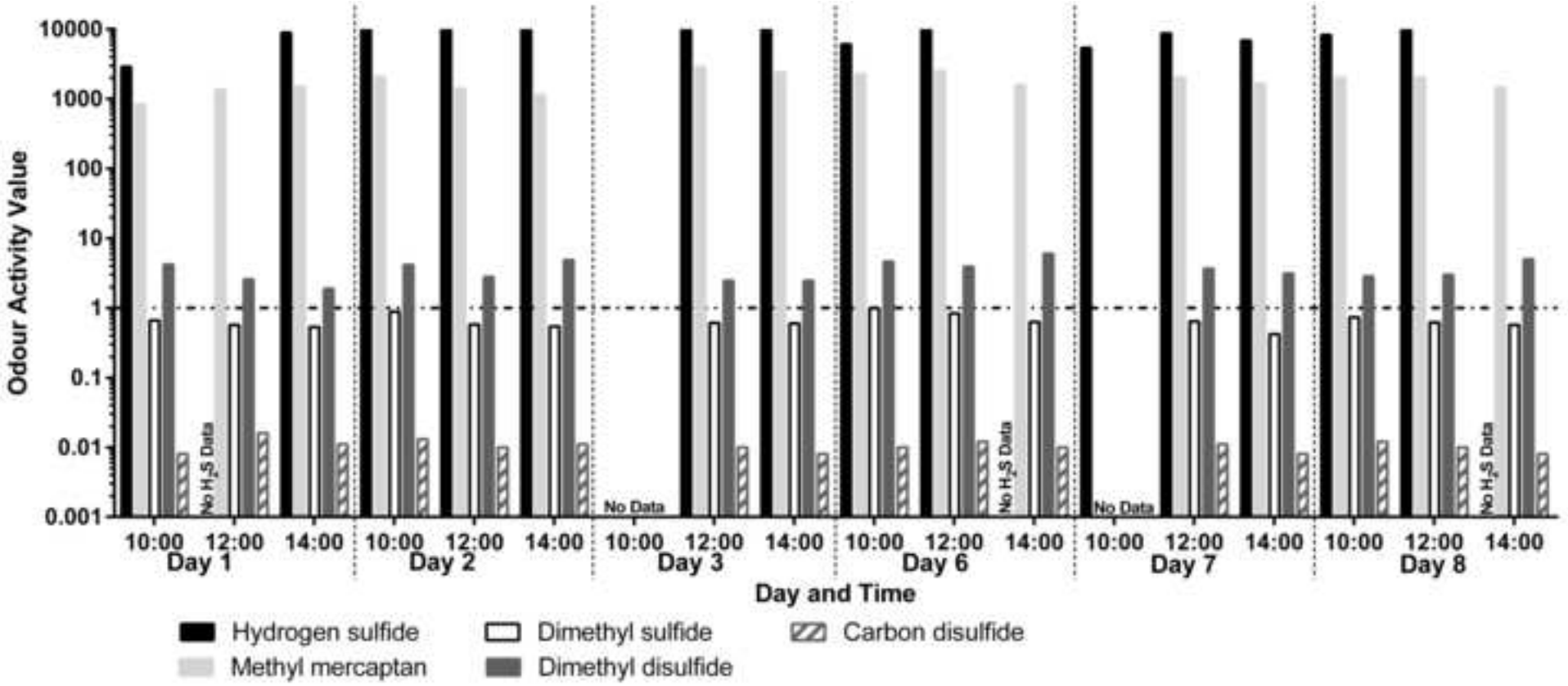

Fig. 4. Daily VOC OAVs - alkanes and halogenated hydrocarbons

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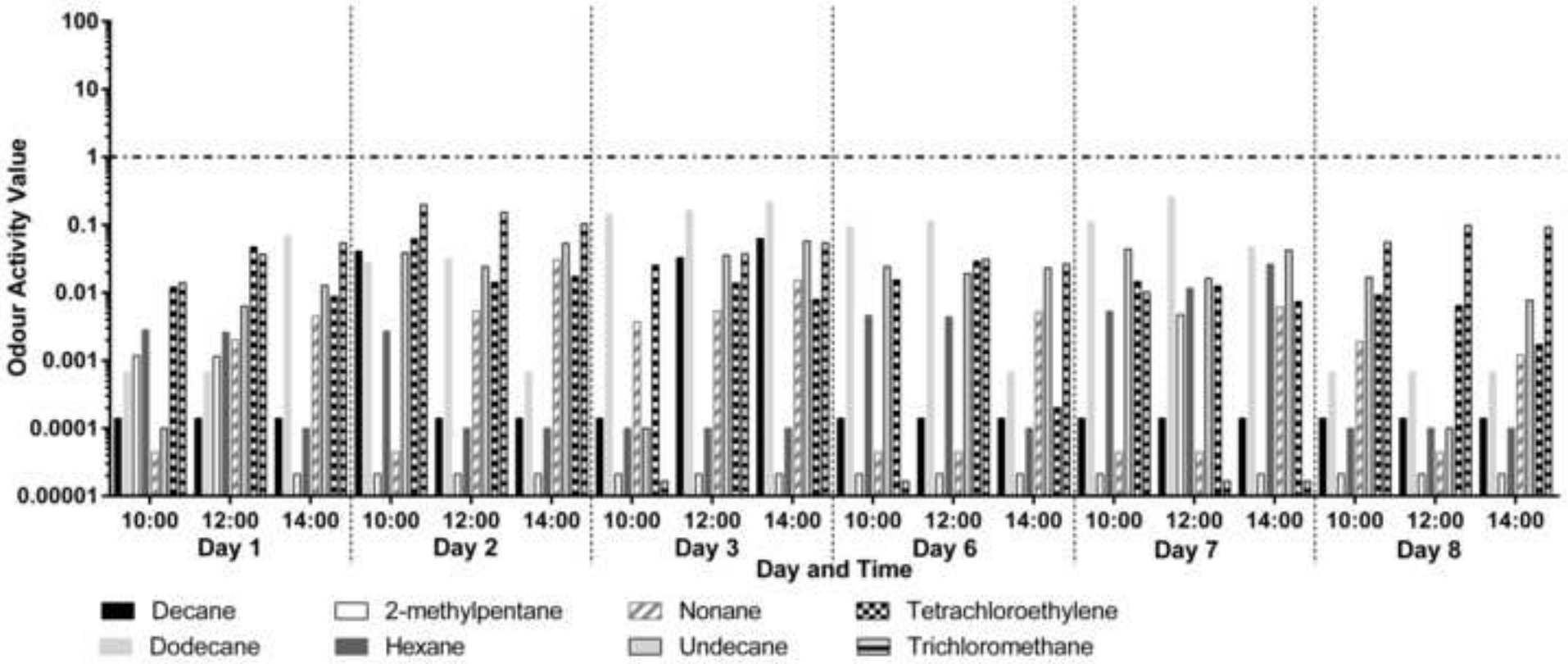

Fig 5. Diurnal variability of VSC OAVs

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